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High temperature electrical transport in gadolinium-iron-transition metal mixed oxides

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Abstract : The paper presents the results of electrical conductivity (σ) and Seebeck coefficient (S) measurements on the pressed pellets of $GdFeTO_4$ (where T = Fe, Cr, Mn, Co and Ni) compounds in the temperature range 400 to 1200 K. It has been shown that these are essentially electronic semiconductors with σ values in the range 10^{-7} to 10^{-3} $\Omega^{-1}m^{-1}$ around 410 K. The maximum value of σ has been observed for $GdFeMnO_4$ and lowest for $GdFe_2O_4$. The log σT *vs* T^{-1} and S *vs* T^{-1} plots yield three temperature regions separated by break temperatures T_1 and T_2. T_1 and T_2 are same in both the plots. The charge carriers are electrons in all temperature ranges. The electrical conductivity in the first range ($T < T_1$) is extrinsic and occurs due to donor type centres. In second ($T_1 < T < T_2$) and third ($T > T_2$) ranges, the electrical conduction is of hopping type and occurs due to hopping of electrons from Fe^{2+} to Fe^{3+} in $GdFe_2O_4$, Co^{2+} or Ni^{2+} to Fe^{3+} in $GdFeCoO_4$ and $GdFeNiO_4$ and from Fe^{2+} to Cr^{3+} centre in $GdFeCrO_4$. In $GdFeMnO_4$, the electrical conduction occurs *via* hopping of electrons from Mn^{3+} to Mn^{4+} centres in $T_1 < T < T_2$ range and from Fe^{2+} to Mn^{3+} centres in $T > T_2$ range

Keywords : Electrical conductivity, Seebeck coefficient, gadolinium-iron-transition metal mixed oxides

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1. Introduction

Mixed rare-earth and transition metal oxides have been the subject of study due to their interesting magnetic, dielectric, electrical transport properties and their applications [1–3]. Several such materials have been investigated by us in the past. Important amongst these are rare-earth iron garnets [4,5], rare-earth orthochromites [6,7], rare-earth vanadates [8,9] and others [10,11]. The 3*d* elements in many of these mixed compounds have variable valence state and yield interesting magnetic, dielectric and electrical transport properties. Expecting some interesting results, we prepared and studied rare-earth-iron-transition metal

mixed oxides and one of these studies is reported in this paper. Going through the literature, we found only limited studies on the compounds of this series. The only studies materials of the entire series are YFe_2O_4, $GdFe_2O_4$ and $LuFe_2O_4$. These studies are related with their preparation and low temperature phase-transition [12,13], neutron diffraction and magnetic properties [14,15], dielectric study [16] and Mössbauer effect [17,18]. Low temperature σ and S data have been explained [19] *via* hopping of electron localized on Fe^{2+} to Fe^{3+} centres. No other study on the electrical transport properties at higher temperature is reported in the literature so far. It has been reported [20–22] that qualitative understanding and semi-quantitative analysis of the conduction mechanism can be presented by studying the electrical conductivity and Seebeck coefficient as a function of various parameters. Using same methodology, we have investigated the electrical transport mechanism of gadolinium-iron-transition metal mixed oxides and the results are reported in this paper.

2. Material preparation and experimental procedure

The starting materials for the preparation of these compounds were Gd_2O_3 [of 99.9% purity, from Johnson Chemical Company, Bombay, India], Fe_2O_3 [of 99.5% purity, from Riedel Dehaen AG, Seelze Hannover, Germany] and oxides Cr_2O_3, NiO, CoO and MnO_2 [of purity, 99.9%, from Rare and Research Chemical, Bombay, India]. The stoichiometric amount of these oxides were mixed and heated in a silica crucible for 50 hrs at a temperature of 1400 K. In this process, mixture was followed by one intermediate grinding and the final product was cool down slowly. The prepared compounds undergo following solid state reaction

$$2\,Gd_2O_3 + 4\,Fe_2O_3 \xrightarrow[\text{Air}]{1400\ \text{K}} 4\,GdFe_2O_4 + O_2,$$

$$2\,Gd_2O_3 + 2\,Fe_2O_3 + 2\,Cr_2O_3 \xrightarrow[\text{Air}]{1400\ \text{K}} 4\,GdFeCrO_4 + O_2,$$

$$Gd_2O_3 + Fe_2O_3 + 2MnO_2 \xrightarrow[\text{Air}]{1400\ \text{K}} 2\,GdFeMnO_4 + O_2,$$

$$Gd_2O_3 + Fe_2O_3 + 2\,CoO \xrightarrow[\text{Air}]{1400\ \text{K}} 2\,GdFeCoO_4,$$

$$Gd_2O_3 + Fe_2O_3 + 2\,NiO \xrightarrow[\text{Air}]{1400\ \text{K}} 2\,GdFeNiO_4.$$

The weight loss corresponding to oxygen on the right hand side of the reactions were observed in all cases except in $GdFeMnO_4$, where the observed loss was slightly less than expected. The details are described elsewhere [23].

To get the confirmation regarding the complete formation of the prepared compounds, X-ray diffraction study have been carried out at room temperature using CuK_α radiation ($\lambda = 0.15418$ nm). From X-ray diffraction pattern, d_{hkl} values have been evaluated using relation

$$d_{hkl} = \frac{0.15418}{2\sin\theta}. \tag{1}$$

From these values of d_{hkl}, structure of the compounds were resolved using usual procedure. All the peaks have been identified and assigned proper hkl values. This confirms that prepared compounds are in single phase. All the compounds have been found to have orthorhombic unit cell with unit cell parameters a_0, b_0 and c_0 as given in Table 1.

Table 1. Structural parameters of the studied $GdFeTO_4$ compounds

Compound	Lattice parameters (nm)			Unit cell volume $m^3 \times 10^{28}$	Calculated density kg $m^{-3} \times 10^3$
	a_0	b_0	c_0		
$GdFe_2O_4$	0.6242	0.7366	0.8836	4.0627	5.44
$GdFeCrO_4$	0.6340	0.7282	0.8858	4.0896	5.34
$GdFeMnO_4$	0.6274	0.7386	0.8856	4.1039	5.37
$GdFeCoO_4$	0.6286	0.7416	0.8924	4.1601	5.36
$GdFeNiO_4$	0.6296	0.7386	0.8878	4.1285	5.40

The measurements of electrical conductivity (σ) and Seebeck coefficient (S) were performed on pressed pellets because of difficulties in growing large single crystal of these compounds needed for such measurements due to their high melting point and our limited facilities. The details of these measurements including electrode preparation *etc* are given elsewhere [7,23].

3. Results

In order to evaluate bulk value of electrical conductivity and Seebeck coefficient of crystalline solid, the study of pellets density, electrical conductivity and Seebeck coefficients have been done as a function of pelletizing pressure. The details are given elsewhere [23]. It has been found that density of pressed pellets (d_p) depends upon pelletizing pressure (P). In all cases density of pellets increases linearly with P upto a value of $P = 5.28 \times 10^8$ Nm^{-2} then the increase becomes slow and it becomes almost constant for $P \geq 6.32 \times 10^8$ Nm^{-2}. The maximum density of highest pressed pellet (d_p) remains less than calculated density (d_0). The difference obviously occurs due to pore fraction (f) which have been determined by the relation

$$f = \frac{d_o - d_p}{d_o}. \tag{2}$$

The values of d_o, d_p and f for the studied materials are given in Table 2.

The pore fraction is small enough to evaluate any bulk parameter by suitable correction. The electrical conductivity of several pellets (σ_p) of each compound made at different P has been measured using similar electrode at a fixed temperature. The log σ_p *vs* P plot for each material shows that it increases with P and tends to become constant for P exceeding 6.32×10^8 Nm^{-2}. This constancy of σ_p with P ensures significant reduction of

grain boundaries but $d_p < d_0$ indicates that crystalline value of σ may be significantly more than σ_p. The estimation of σ from maximum value of σ_p has been done using relation [7,24]

$$\sigma = \sigma_p \left[1 + \frac{f}{1 + f^{2/3}}\right]. \tag{3}$$

Seebeck coefficient (S) has also been measured for number of pellets of each compound made at P ranging from 3.12×10^8 to 8.4×10^8 Nm^{-2}. Within our experimental accuracy we do not observe any dependence of S on P. This has been true for all compounds. Hence S needs no correction for crystalline solid. This is logically expected because S measurement involves measurement of voltage across the sample pellet when current flow is zero, hence pore fraction does not come in the picture.

Table 2. The calculated density (d_0), pellet density (d_p) of highest pressed pellet and pore fraction (f) of studied compounds

Compound	$d_p \times 10^{-3}$ (Kg m^{-3})	$d_0 \times 10^{-3}$ (Kg m^{-3})	f
$GdFe_2O_4$	4.79	5.44	0.120
$GdFeCrO_4$	4.50	5.34	0.157
$GdFeMnO_4$	4.60	5.37	0.143
$GdFeCoO_4$	4.55	5.36	0.151
$GdFeNiO_4$	4.70	5.40	0.130

Electrode play an important role in the measurement of σ. For such measurement Ohmic contact between the pellet and electrode interface is essential [25]. Even in the case of Ohmic contact, contact resistance play an important role in σ measurement [25]. To ensure Ohmic contact, we have measured current through the pellet at different applied voltages at constant temperature. Using dimension of the pellet, current density (J) and electric field (E) have been evaluated. It has been found that for pellet of studied material J *vs* E plots are straight line upto $E \sim 6.0 \times 10^3$ V/m, ensuring Ohmic contact between pellet and electrode interface.

Since several superfluous effects not connected with bulk property of the material can arise due to grain boundaries, it is essential to see that grain boundary effects have been minimized in highly pressed pellets made using very fine grain powders. This can be done by measuring σ at different ac signal frequencies and seeing that it does not depend upon it. To do that σ_p has been measured at dc = 100 Hz, 1 KHz and 10 KHz; and a plot of log σ_p *vs* log f has been obtained. It has been observed that log σ_p is independent of log f. The dc and ac values of σ_p have been found to be the same. This indicates that grain boundary effects are considerably minimized in highly pressed pellets.

The dc current density through the pellet of all studied materials have been measured as a function of time at constant temperature and applied dc field. It is found that J is independent of time. This observation indicates that the electrical conductivity of studied compounds is essentially electronic and ionic conductivity is negligibly small.

The electrical conductivity (σ) measurement of few pellets of each studied material has been carried out in the temperature range 400 K to 1200 K. The measurements have been done on pellets made at $P > 6.32 \times 10^8$ Nm $^{-2}$ and sintered around 1000 K for 50 hrs. The σ_p values do not differ for different samples and are also independent of pellet dimensions. Further, no difference in σ_p values have been found during heating and cooling cycles.

It also remains almost same irrespective of thermal history and shelf life of the pellet. The mean value of σ_p for few pellets of each compound has been taken as the bulk value of σ_p. The σ value have been evaluated using eq. 3. The plots of log σT *vs* inverse of absolute temperature (T^{-1}) for different studied materials are shown in Figures (1–5). It is

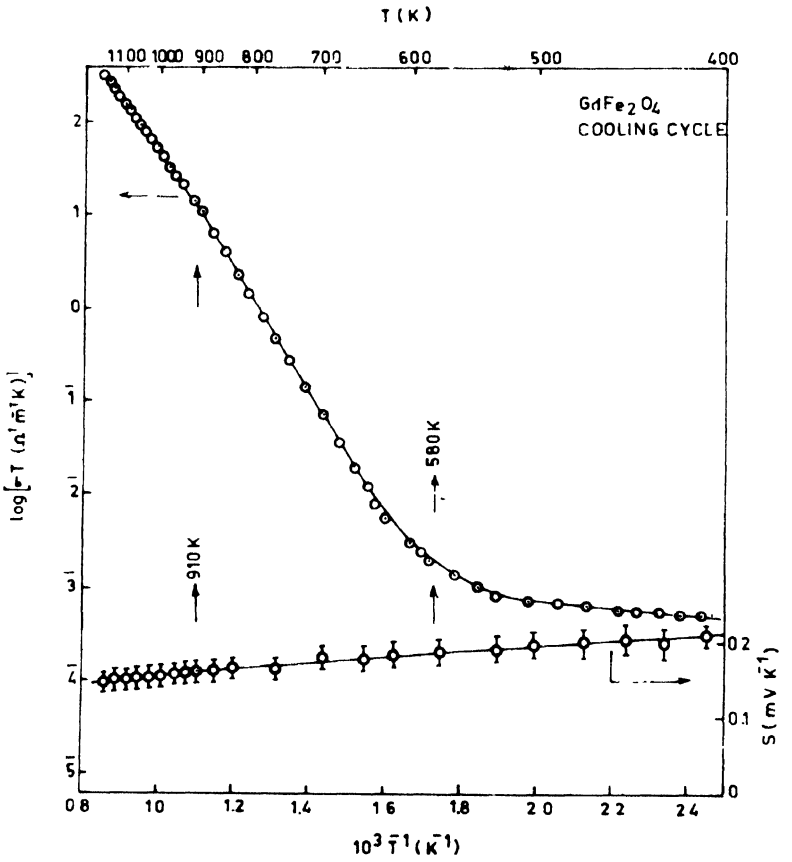

Figure 1. Plots of logarithm of product of electrical conductivity and temperature (log σT) and Seebeck coefficient (S) against inverse of absolute temperature (T^{-1}) for $GdFe_2O_4$

seen from these figures that each plot can be divided into three linear regions namely range I for $T < T_1$, range II for $T_1 < T < T_2$ and range III $T > T_2$. T_1 and T_2 have been termed as break temperatures. In each region, the variation of log σT *vs* T^{-1} can be represented by the relation

$$\sigma T = \sigma_0 T \exp\left(-E_a/kT\right). \tag{4}$$

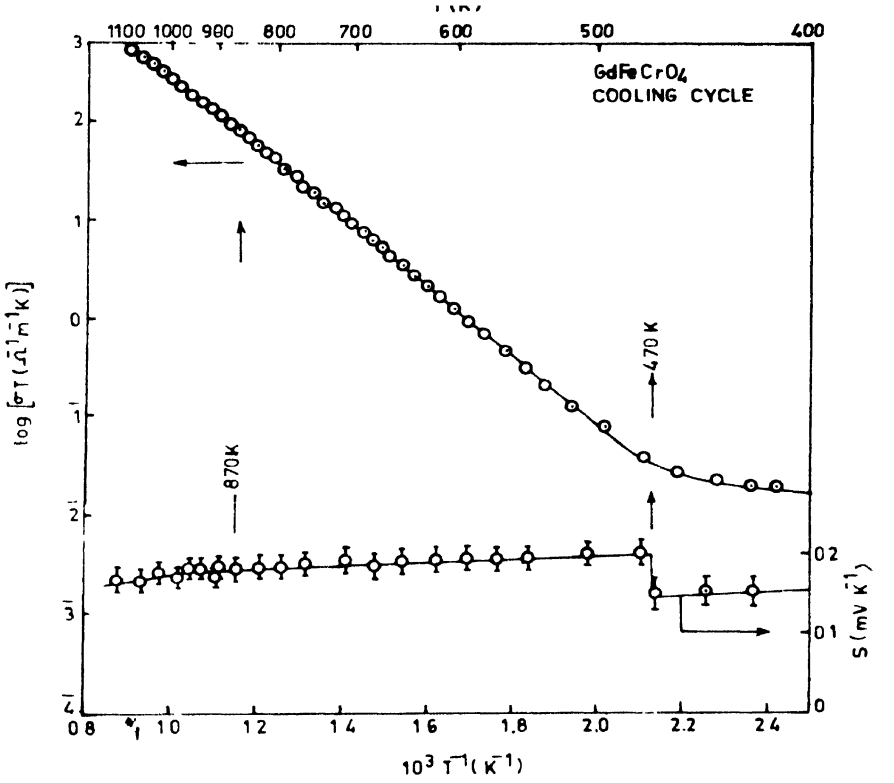

Figure 2. Same as Figure 1 for $GdFeCrO_4$

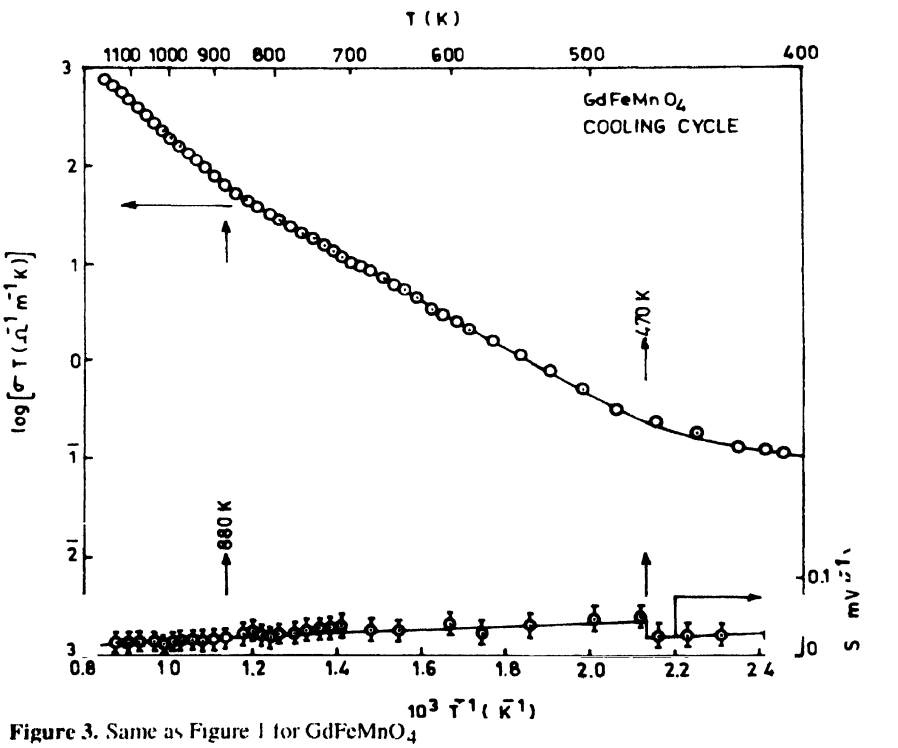

Figure 3. Same as Figure 1 for $GdFeMnO_4$

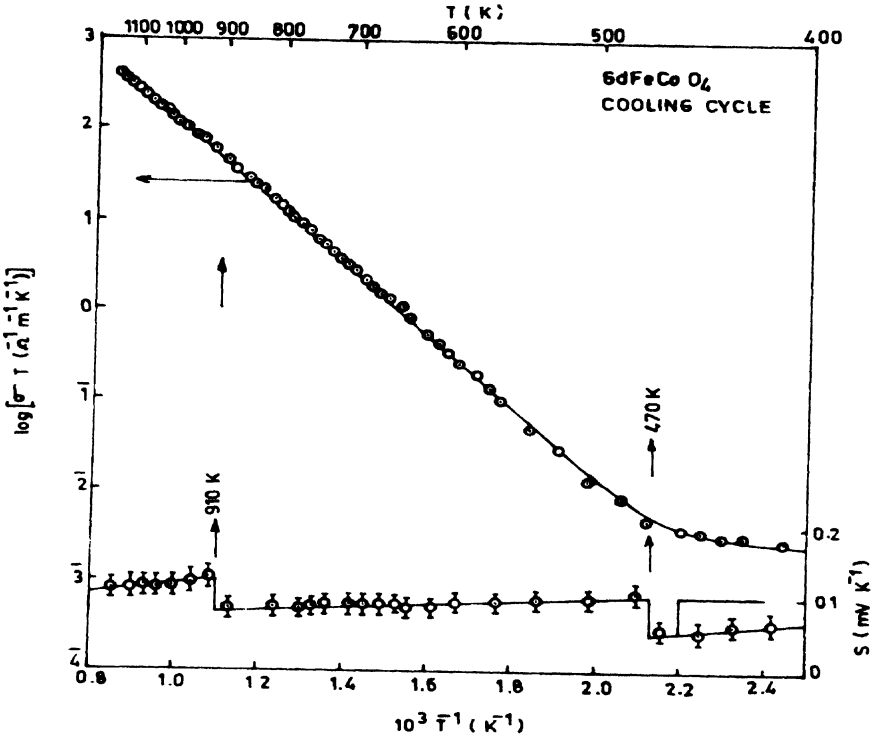

Figure 4. Same as Figure 1 for $GdFeCoO_4$

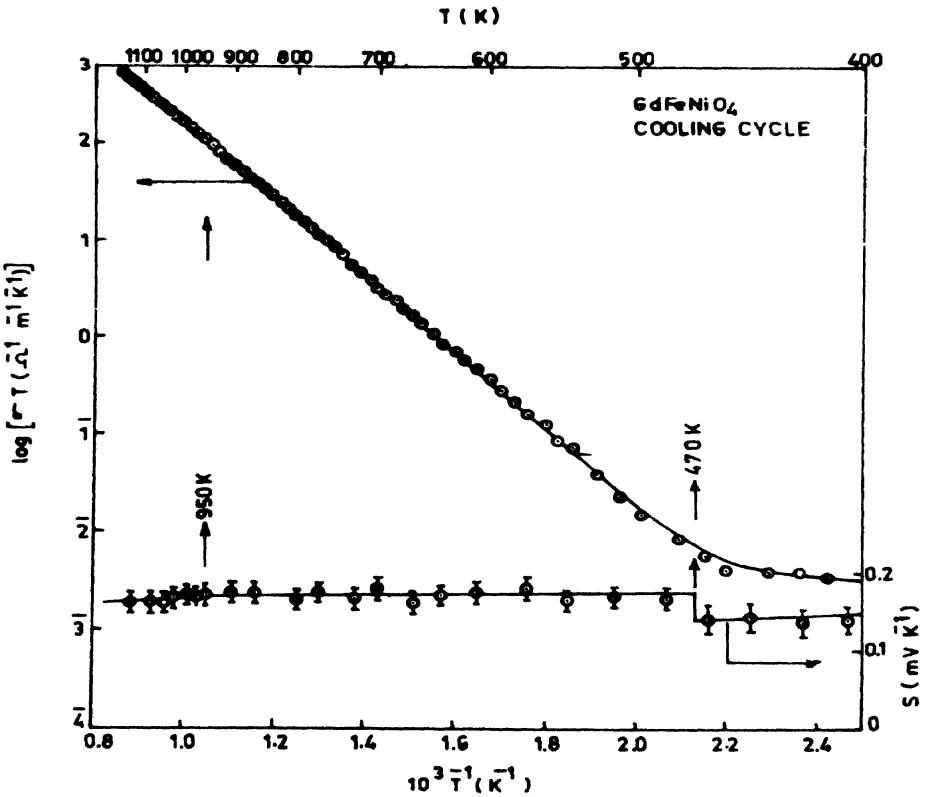

Figure 5. Same as Figure 1 for $GdFeNiO_4$.

The values of pre-exponential constant ($\sigma_0 T$) and activation energy (E_a) have been evaluated from the experimental plot and are given in Table 3 together with the values of T_1 and T_2.

Table 3. Values of pre-exponential constant ($\sigma_0 T$) and E_a together with T_1 and T_2 in different regions of log σT *vs* T^{-1} plots of studied compounds.

Compound	For $T < T_1$			For $T_1 < T < T_2$			For $T > T_2$	
	$\sigma_0 T$ ($\Omega^{-1}m^{-1}K$)	E_a (eV)	T_1 (K)	$\sigma_0 T$ ($\Omega^{-1}m^{-1}K$)	E_a (eV)	T_2 (K)	$\sigma_0 T$ ($\Omega^{-1}m^{-1}K$)	E_a (eV)
$GdFe_2O_4$	4.56×10^{-3}	0 08	580	3.36×10^{8}	1 34	910	3.67×10^{7}	1.17
$GdFeCrO_4$	$2\ 21 \times 10^{-1}$	0 09	470	1.29×10^{6}	0 72	870	5.54×10^{5}	0.66
$GdFeMnO_4$	$1\ 09 \times 10^{-1}$	0 16	470	3.04×10^{4}	0.48	880	2.03×10^{6}	0.80
$GdFeCoO_4$	$7\ 72 \times 10^{-2}$	0 12	470	$1\ 40 \times 10^{6}$	0.80	910	$5\ 45 \times 10^{5}$	0 73
$GdFeNiO_4$	$3\ 52 \times 10^{-2}$	0 08	470	$1\ 93 \times 10^{6}$	0 80	950	$8\ 42 \times 10^{5}$	0 74

The Seebeck coefficient measurements on different pellets of each material have also been done. These values do not differ from sample to sample and are also independent of pellet dimension within experimental accuracy which is about ± 10% around 800 K and reduces to ± 5% around 1000 K. These are nearly same in heating and cooling cycles. The repeated values of S has been recorded for each material in the temperature range 400 to 1200 K and have been presented in Figures (1–5) as S *vs* T^{-1} plot. We must point out at this stage that standard convention for the values of S have been used. In this convention, $S = \frac{\Delta E}{\Delta T}$ and has positive sign for negative charge carrier and *vice-versa*. It is observed for S *vs* T^{-1} plot that S values are positive throughout the studied temperature range indicating dominance of negative charge carrier in the conduction. S *vs* T^{-1} plots can be divided into three linear regions namely range I for $T < T_1$, range II for $T_1 < T < T_2$ and range III for $T > T_2$; T_1 and T_2 being the break temperatures. In each range, plot of S *vs* T^{-1} can be represented by the relation

$$S = \frac{\eta}{eT} + H, \tag{5}$$

where η and H are constants for each region. The values η, H, T_1 and T_2 are given in Table 4.

4. Discussion

As mentioned in the previous section, σ_{dc} has been found independent of time even at relatively higher temperature and for sufficiently long time. Further, no significant difference has been found in σ_{ac} and σ_{dc} values. Also σ_{ac} has been found independent of ac signal frequencies. All these observations indicate that studied materials are essentially electronic conductors and ionic conductivity, if any, is significantly small. The Seebeck coefficient has been found positive throughout the studied temperature range. Thus, electrons are the majority charge carrier in these materials. Around 410 K, σ of studied

compounds lies in the range 10^{-7} to $10^{-3}\ \Omega^{-1}m^{-1}$ and increases with increase of temperature. Thus, studied compounds are typical semiconductor. The log σ *vs* T^{-1} as well as S *vs* T^{-1} plots have three linear regions separated by break temperature T_1 and T_2. The temperatures

Table 4. Constants η and H for different regions together with the values of T_1 and T_2 for the studied compounds

Compound	For $T < T_1$			For $T_1 < T < T_2$			For $T > T_2$	
	η (eV)	H (mV K^{-1})	T_1 (K)	η (eV)	H (mV K^{-1})	T_2 (K)	η (eV)	H (mV K^{-1})
$GdFe_2O_4$	0.033	0.131	580	0.040	0.117	910	0.056	0.099
$GdFeCrO_4$	0.025	0.091	470	0.017	0.162	870	0.068	0.102
$GdFeMnO_4$	0.020	−0.020	470	0.025	−0.008	880	0.025	−0.009
$GdFeCoO_4$	0.048	−0.050	470	0.024	0.054	910	0.063	0.057
$GdFeNiO_4$	0.022	0.093	470	0.006	0.162	950	0.046	0.121

T_1 and T_2 have been found to be nearly same in σ as well as S plots. No phase change have been reported in these compounds in the studied temperature range. Thus, these break temperatures indicate the change in conduction mechanism in these solids. The values of E_a (~ 0.1 eV) in first temperature range ($T < T_1$) is small for all studied materials. The value of pre-exponential constant ($\sigma_0 T$) in this range is also small (~ $10^{-2}\ \Omega^{-1}m^{-1}K$). Both these values are not appropriate for intrinsic conduction. Thus we conclude that for $T < T_1$, the electrical conduction in these materials is extrinsic and is due to impurities or defects However, at $T > T_1$; E_a as well as $\sigma_0 T$ values are large indicating intrinsic conduction

For $T < T_1$, the electrical conduction is extrinsic and thus in order to explain it, one has to look for possible defects and impurities. A chemical impurity of the order of 0.1 percent is expected in these materials. This has been inferred from the stated purity of the materials used for the preparation of these compounds. In order to resolve the conduction mechanism, the appropriate plots are log σ *vs* T^{-1} and S *vs* T^{-1} plot. For donor type impurity centres, band conduction yield a conductivity expression $\sigma = \sigma_0 \exp(-Ed/kT)$, where Ed is donor ionization energy. For this type of conduction, the slope of S *vs* T^{-1} and log σ *vs* T^{-1} plot should be same [22]. The slope of log σ *vs* T^{-1} can be inferred from the slope of log σT *vs* T^{-1} plot given in Table 3. However, we have obtained these slopes (values of Ed's) by drawing log σ *vs* T^{-1} plot which are not presented in the paper. These are given in Table 5.

It is seen from Table 5 that the slope of S *vs* T^{-1} plot η and log σ *vs* T^{-1} plot Ed have nearly the same value (taking errors in the values) for all except $GdFeMnO_4$. This indicates that extrinsic conduction in all other materials is due to donor type impurities. No exact reason can be given for the extrinsic conduction in $GdFeMnO_4$. However, it may be remarked that in the preparation of $GdFeMnO_4$, the observed oxygen-loss is less than expected as indicated in reaction 3. Thus, some excess oxygen is left in the sample. This oxygen converts itself into O^{2-} ion by taking an electron each from Mn^{3+} center and converting two of them in Mn^{4+} center. The distance between the oxygen ion and Mn^{3+}

center for this process should be small. With this configuration, natural hopping of electron from O^{2-} to Mn^{4+} center is expected with lower activation energy. The E_a = 0.16 eV is probably due to this process. The process appears more probable in view of the fact observed electrical conductivity for this compound is highest amongst the studied compounds and slope of S *vs* T^{-1} ($\eta \sim 0.02$) plot is very small. However, the discussion should not be extended any further.

Table 5. Values of Ed and η for the studied materials. The values E_a from Table 3 are also listed for the reference.

Compound	E_a (eV)	Ed (eV)	η (eV)
$GdFe_2O_4$	0.08	0.03	0.033
$GdFeCrO_4$	0.09	0.04	0.025
$GdFeMnO_4$	0.16	0.10	0.020
$GdFeCoO_4$	0.12	0.06	0.048
$GdFeNiO_4$	0.08	0.03	0.022

In intrinsic range, the majority charge carriers are electrons as indicated by positive value of Seebeck coefficient. $GdFe_2O_4$ is essentially an ionic compound as has been concluded by us on the basis of magnetic susceptibility studies [23]. Thus, the material will contain Gd^{3+}, Fe^{2+} and Fe^{3+} ions. Fe is multivalent and it is natural to think that conduction in this compound occurs *via* hopping of electrons localized on Fe^{2+} to Fe^{3+} sites. The hopping of electrons in $LuFe_2O_4$ has already been observed through Mossbaur studies [17,18] and data of σ and S have been explained using this mechanism [19].

The activation energy for hopping is 1.34 eV. The Seebeck coefficient S in hopping motion is given by the expression [26].

$$S = \frac{k}{e}\left[\frac{S_R^*}{k} - \log_e\left(\frac{c}{1-c}\right)\right] \tag{7}$$

where S_R^* is the effective entropy of the lattice which is temperature independent and $c = n/N$, where n and N are the densities of defects and normal sites respectively. In $GdFe_2O_4$, $n = N/2$ giving $c = 1/2$ and logarithmic terms of S to be zero. Hence

$$S = \frac{S_R^*}{e}. \tag{8}$$

Thus, S should be temperature independent. Experimental values of S in $GdFe_2O_4$ for $T > T_1$, are small and temperature independent which supports the hopping mechanism.

In $GdFeCoO_4$ and $GdFeNiO_4$, ions are Gd^{3+}, Fe^{3+} and Co^{2+} and Ni^{2+} as concluded by our magnetic susceptibility (χ_m) studies [23]. The electrical conduction in intrinsic range in these compounds should occur *via* hopping of electrons from Co^{2+} or Ni^{2+} centers to Fe^{3+} centers. The activation energy of hopping in these compounds is 0.80 eV. S has also been found nearly temperature independent as expected.

$GdFeCrO_4$ is also ionic with Gd^{2+}, Fe^{2+} and Cr^{3+} as its constituent ions as concluded by our susceptibility study. The hopping conduction in this material will occur due to hopping of electrons from Fe^{2+} to Cr^{3+} sites. The activation energy is 0.72 eV.

In all the three compounds discussed above, the slope of log σT *vs* T^{-1} plot drops for $T > T_2$. This is due to smoothing of potential barrier or thermal fluctuations as observed in other materials [27].

In case of $GdFeMnO_4$, the expected ions are Gd^{3+}, Fe^{2+} and Mn^{3+}. S is constant and positive. Thus, normal conduction in this solid should be due to hopping of electrons from Fe^{2+} to Mn^{3+} centres. But observed activation energy E_a is small (0.48 eV). Further for $T > T_2$, E_a goes up against the decrease observed in other compounds. Thus in this compound, hopping mechanism appears due to different kind of centers. In this regard, it is to be noted that the starting material for the preparation of this compound is MnO_2. Thus Mn^{3+} centers can be formed only when excess oxygen is liberated in the formation of the compound. But it has not been found true experimentally. Thus, existence of both Mn^{4+} and Mn^{3+} centres are expected in this compound together with the excess of oxygen. The value of electrical conductivity of this compound has been found higher in the studied series. The extra defects are responsible for higher conductivity. For the temperature range $T_1 < T < T_2$, the conduction mechanism in view of above facts, appears to be due to the hopping of electrons from Mn^{3+} to Mn^{4+} centres. At much higher temperature, the hopping of electrons from Fe^{2+} to Mn^{3+} centres takes over the conduction mechanism. The activation energy in latter case is larger in comparison to former.

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